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OKADA KOJI**(54) ALUMINUM ALLOY CLAD MATERIAL FOR HEAT EXCHANGER**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an Al alloy clad material having improved corrosion resistance by cladding one side of an Al alloy core material with a specified Al alloy as a sacrificial anode material and the other side with an Al-Si alloy as a brazing filler metal.

SOLUTION: One side of an Al alloy core material is clad with an Al alloy consisting of 1.0-6.0 wt.% Zn, 0.2-2.0 wt.% Mn and the balance substantially Al as a sacrificial anode material and the other side is clad with a brazing filler metal. The cladding Al alloy contains an Al-Mn intermetallic compd. of 0.1-0.8 μ m average grain diameter at $\geq 2.0 \times 10^9$ grains/mm³ density. In the alloy, Zn satisfactorily enhances sacrificial anticorrosive effect in any of acidic and alkaline corrosive environments and Mn regulates the distribution of the Al-Mn intermetallic compd. and inhibits erosion-corrosion. The core material is not particularly limited and it is based 011 3003 alloy, etc. The brazing filler metal is not particularly limited and it is, e.g. an Al-Si alloy stipulated by JIS 4343.

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CLAIMS

[Claim(s)]

[Claim 1] To each one side of aluminum alloy core material, it is Zn. 1.0 - 6.0%, Mn 0.2 - 2.0% (% shows weight % above.) is contained. It is number density 2.0×10^9 about the aluminum-Mn system intermetallic compound whose mean particle diameter it is Remainder aluminum and aluminum alloy which consists of an unescapable impurity in addition to this, and is 0.1-0.8 micrometers. An individual / mm³ Sacrificial anode material which consists of an aluminum alloy contained above, Aluminium alloy composite for heat exchangers characterized by coming to carry out the clad of the wax material of the aluminum-Si system alloy containing Si of the specified quantity.

[Claim 2] aluminum alloy of the above-mentioned sacrificial anode material is In. 0.005 - 0.5%, Sn 0.005 - 0.5%, Si 0.02 - 1.2%, germanium Aluminium alloy composite for heat exchangers according to claim 1 characterized by containing two of one sort or 0.005 - 2.0% of sorts or more.

[Claim 3] The corrosion current value of said sacrificial anode material is 40microA/cm². Aluminium alloy composite for heat exchangers according to claim 1 or 2 characterized by being the following.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to aluminum alloy composite of a three-tiered structure suitable as an ingredient of tube tubing which forms the refrigerant path of the heat exchanger which would stretch in more detail and was formed of law about aluminum alloy composite of the thin meat used for the heat exchanger for automobiles etc.

[0002]

[Description of the Prior Art] One example of the usual heat exchanger made from aluminum, for example, a radiator, is shown in (b) of drawing 1, and (b). As (b) of drawing 1 is a front view, (b) is the A-A line sectional view of (b) and it is shown in this drawing, this radiator arranges a fin 2 between the tube tubing 1 which lets a refrigerant pass, attaches the header plate 3 in the both ends of the tube tubing 1, assembles a core 4 and comes to attach the resin tank 5 and 5' in the header plate 3 after soldering through packing 6. On a fin 2, in order to prevent pitting generating by the side of a refrigerant in tube tubing at a JIS3003 alloy presentation using the plate around 0.1mm in thickness which carried out extent addition of the Zn 1.5% (especially % that shows a presentation unless it refuses says weight % hereafter.) A brazing sheet with a thickness of 0.3-0.2mm which made the alloy which added Mg etc. sacrificial anode material, and carried out the clad to the JIS3003 alloy presentation inside the alloy core material which added Si, Cu, etc. (refrigerant side) at JIS7072 alloy or it is used. The brazing sheet of the same quality of the material as the tube tubing 1 with a thickness of 1.0-1.3mm is used for the header plate 3.

[0003] These brazing sheets are exposed to an about 580-610-degree C ambient atmosphere at the time of soldering heating, and this diffuses Zn in the above-mentioned sacrificial anode material in a core material. Drawing 2 shows this condition and (b) of drawing 2 of (b) of drawing 2 is after soldering before soldering. Since this Zn diffusion layer carries out priority corrosion, pitting generated from a refrigerant side does not grow deeply, but takes a shallow large pitting gestalt, and comes to show long-term pitting-proof nature. An aluminum-Zn system, an aluminum-Zn-Mg system, or the aluminum-Mg-In system sacrificial anode alloy itself has the description which takes a shallow large pitting gestalt (page foods), further, even after a core material is exposed, sacrificial anode material is preferentially corroded by the potential difference of a core material and these sacrificial anode material, and it prevents the corrosion of a core material according to it.

[0004] As such conventional aluminium alloy composite, Zn and Mn of the specified quantity are made to contain, and the technique using the sacrificial anode material of the aluminium alloy which improved reinforcement is proposed (JP,56-127194,A, 58-113367, etc.). However, Mn in sacrificial anode material is for making potential for the improvement in on the strength into **, and does not aim at corrosion resistance improvement. However, by one side of the board thickness reduction accompanying the latest lightweight-izing, with advanced features of a heat exchanger, the liquid rate of flow inside tube tubing is very quick compared with the former, and corrosion prevention effectiveness sufficient in the above conventional sacrificial anode material is no longer acquired. That is, since a corrosion rate is

increased the more the more the liquid rate of flow inside tube tubing becomes quick, development of the aluminium alloy composite material which can respond to this and in which higher corrosion resistance (self-corrosion resistance or sacrifice anti-corrosiveness) is shown is demanded.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the aluminium alloy composite for heat exchangers which raised corrosion resistance further. The purpose of this invention aims still more detailed at providing the bottom of the rise of the liquid rate of flow with the aluminium alloy composite for pile heat exchangers for an erosion corrosion phenomenon at a lifting in the refrigerant side environment of a tube inside.

[0006]

[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, after specifying Zn of sacrificial anode material, and the amount of Mn By controlling the particle size of the aluminum-Mn system compound in sacrificial anode material, and distribution The corrosion current value accompanying a corrosion prevention operation of sacrificial anode material can be reduced, and this cannot cause erosion corrosion easily under the large environment of the rate of flow. The function of sacrificial anode material is maintained for a long period of time, it finds out raising corrosion resistance sharply and getting, research is further repeated in this knowledge, and it came to make this invention. That is, this invention is Zn to each one side of (1) aluminum alloy core material. 1.0-6.0%, Mn 0.2-2.0% (% shows weight % above.) It contains and they are Remainder aluminum and aluminum alloy which consists of an unescapable impurity in addition to this. And it is number density 2.0×10^9 about the aluminum-Mn system intermetallic compound whose mean particle diameter is 0.1-0.8 micrometers. An individual / mm³ Sacrificial anode material which consists of an aluminum alloy contained above, The aluminium alloy composite for heat exchangers characterized by coming to carry out the clad of the wax material of the aluminum-Si system alloy containing Si of the specified quantity, (2) aluminum alloy of the above-mentioned sacrificial anode material 0.005 - 0.5% of In(s), Sn 0.005 - 0.5%, 0.02 - 1.2% of Si, germanium Aluminium alloy composite for heat exchangers given in (1) term characterized by containing two of one sort or 0.005 - 2.0% of sorts or more, (3) -- the corrosion current value of said sacrificial anode material -- 40microA/cm² The aluminium alloy composite for heat exchangers (1) characterized by being the following or given in (2) terms is offered. [and] Suppressing low the corrosion dissolution (corrosion current) of sacrificial anode material according to this invention, the corrosion prevention of the core material is carried out efficiently, and erosion can be controlled. In this invention, by specifying the magnitude of the aluminum-Mn system compound in sacrificial anode material, and distribution, it is effective in reducing the corrosion current value of sacrificial anode material remarkably, and can be hard to cause erosion corrosion for the inside of a tube also under the large operating environment of the rate of flow of flowing fluid by this, the function of sacrificial anode material can be maintained for a long period of time, and corrosion resistance can be raised sharply.

[0007]

[Embodiment of the Invention] The sacrificial anode material used in this invention is excellent in a corrosion resistance (self-corrosion resistance and sacrifice anti-corrosiveness) operation. Zn in sacrificial anode material may be 1.0 - 6.0%. Corrosive environment enlarges [Zn] the sacrifice corrosion prevention effectiveness enough also in any by the side of acidity or alkalinity. The addition of Zn cannot maintain sacrifice corrosion prevention ability in an acid environment especially at less than 1.0%. In exceeding 6.0%, there is a possibility that there may be a possibility that oxide film depressor effect and the sacrifice corrosion prevention ability maintenance effectiveness may fall sharply in an alkaline environment, and ingredient melting may occur near the interface of sacrificial anode material and a core material depending on the temperature at the time of soldering heating. Zn addition is 2.5% - 4.5% preferably.

[0008] Mn may be 0.2 - 2.0%. Mn regulates aluminum-Mn system compound distribution, and acts on solution of the problem of erosion corrosion. Mn is because there is a possibility of causing the problem of a weld flaw (micro fissure) or a poor bending processing dimension, at less than 0.2% when the

above-mentioned effectiveness is not fully demonstrated, but exceeds 2.0% and tube tubing is manufactured by **** processing or bending soldering processing. In this invention, mean particle diameter of the aluminum-Mn system intermetallic compound in sacrificial anode material is set to 0.1-0.8 micrometers, and it is that number density 2.0×10^9 An individual / mm³. Because this compound distribution out of range of the effectiveness which reduces the corrosion current accompanying the corrosion prevention of sacrificial anode material, and controls erosion corrosion is insufficient, it considers as the above. In this invention, by doing in this way, as mentioned above, a sacrifice material corrosion current value can be controlled more remarkably than the value of the conventional sacrificial anode material, and it can decrease. The electrochemistry measurement result of the sacrificial anode material of this invention is shown in drawing 3 as a mimetic diagram. From drawing 3, by controlling distribution of an aluminum-Mn compound in the range of this invention shows that the so-called corrosion current equivalent to the intersection of an anode curve and a cathode curve decreases remarkably. The corrosion current value of sacrifice material is 40microA/cm². If it is the following, the above-mentioned effectiveness will be demonstrated. A and B show the anode of the example of this invention, and the conventional example, and the intersection of a cathode bipartite polar curve among drawing 3, respectively, and this invention has this intersection in left-hand side from a dotted line C (equivalent to 40micro A/cm² of currents). The corrosion resistance which was excellent for a long period of time can be maintained by carrying out the specified quantity selection convention of In, Sn, and the germanium to sacrificial anode material further depending on corrosive environment in this invention. 0.005 - 2.0% of germanium addition is desirable. At less than 0.005%, it becomes difficult for there to be almost no effectiveness which controls oxide film formation of a sacrificial anode material front face under an alkaline environment, therefore to maintain sufficient sacrifice corrosion prevention function. Even if it exceeds 2.0%, the above-mentioned effectiveness not only does not improve any more, but the rolling nature at the time of ingredient manufacture and the yield fall, and the problem on mass production comes out. More desirable germanium addition is 0.2 - 1.5%. The effectiveness of In and Sn addition is the same as that of Zn. Less than by 0.005, the sacrifice effectiveness runs short, when 0.5% is exceeded, the rolling nature at the time of ingredient manufacture falls, and there is a possibility that the problem that a coil end breaks may occur. In addition, these additions are 0.02 - 0.2% preferably. Moreover, if it carries out sacrificial anode material by addition of Si and is, the reinforcement of composite rises, and it contributes to the improvement in endurance of a heat exchanger. Having made the addition into 0.02 - 1.2% has a possibility of causing deep pitting by the simple substance Si, when less than 0.02 are insufficient as for the above-mentioned effectiveness and 1.2% is exceeded. A more desirable addition is 0.3 - 0.7%.

[0009] In this invention, there is especially no limit about a core material. Improvement in on the strength may be aimed at by Si, Cu, and Mn addition based on a 3003 alloy presentation. Cr, Zr, Mg, and Ti may also be suitably added for the purpose of the improvement in on the strength. As wax material in this invention, there is especially no limit, for example, it can use JIS [of an aluminum-Si system]4343, and JIS4045 alloy, JIS4004 alloy, etc.

[0010] Such heat exchanger aluminium alloy composite can be prepared as follows. Control of the aluminum-Mn system intermetallic-compound distribution in sacrificial anode material is realizable by performing homogenization temperature before sacrificial anode material rolling at 440-520 degrees C. It is difficult to equalize an ingot organization at less than 440 degrees C. In carrying out exceeding 520 degrees C, big and rough-ization of a compound becomes active, and it becomes difficult to carry out distribution as the above-mentioned convention of this invention. The holding time in the above-mentioned temperature has 3 - 9 desirable hours. Not only the homogenization temperature of sacrificial anode material but a convention of the clad rolling initiation temperature which is a process after that is important, and clad temperature is good to carry out at 420-520 degrees C. There is a possibility that the phenomenon in which sacrificial anode material separates [this temperature] from a core material at less than 420 degrees C at the time of clad rolling may come out. Although there is no problem of poor clad sticking by pressure when carrying out exceeding 520 degrees C, it becomes difficult to satisfy compound distribution of the sacrificial anode material specified by this invention. In addition, cold

rolling and especially intermediate-annealing conditions are not limited.

[0011] aluminum alloy composite of this invention can be used also for the header plate of a radiator besides radiator tube tubing, in addition if it is the same as that of the purpose of this invention, it can fully be used also as the tube seat of what kind of member, for example, a heater core, or a DORON cup evaporator, and header tubing. In the aluminium alloy composite of this invention, although especially a limit does not have the rate of a clad of sacrificial anode material, 8 - 20% is desirable to all composite board thickness (by thickness), and 12 - 17% is more desirable. Moreover, the rate of a clad of wax material does not differ especially from the conventional thing, but is usually 8 - 12% preferably 5 to 15% to all composites. Although the thickness of the heat exchanger aluminium alloy composite of this invention changes with classes of an application and heat exchanger etc., it is usually 0.2-0.4mm.

[0012]

[Example] Next, this invention is further explained to a detail based on an example.

Metal mold casting cast 17 kinds of combination alloys of the sacrificial anode material of a presentation, and a core material shown in example 1 table 1, sacrificial anode material homogenized after double-sided facing respectively on the conditions shown in Table 2, and 40mm was made to 5mm in thickness, and a core material only by facing with hot rolling. That is, it was made for the rate of a clad to the whole (for wax material to also be included) composite of sacrificial anode material to become 10%. In addition, comparison sample No.18 in Table 2 are completely the same as that of sample No.3 of this invention except having changed homogenization of sacrificial anode material like a notation in alloy No.3 of this invention. Using JIS4343 alloy, metal mold casting of the wax material was carried out like sacrificial anode material, and after facing, it performed hot rolling and was taken as 5mm thickness. That is, the rate of a clad to the whole composite was made into 10%. Hot rolling was started on the conditions which show repeatedly three sheets, wax material, a core material, and sacrificial anode material, in Table 2 at this order, and it considered as the clad plate with a thickness of 3.5mm of three layers. It considered as 0.29mm thickness with cold rolling after that, and intermediate annealing of 340 degree-Cx 2 hours was given, and, finally it cold-rolled to 0.25mm in thickness, and considered as the sample of H14 material. About aluminum-Mn system intermetallic-compound number density with a mean particle diameter [in sacrificial anode material] of 0.1-0.8 micrometers, the flake was perpendicularly cut [samples / these] down to the rolling direction by the precision cutter (microtome equipment), and it measured with the transmission electron microscope. Then, sample thickness was determined by the fringes of equal thickness, and mean particle diameter calculated the number density of the thing of the aluminum-Mn system compound which is 0.1-0.8 micrometers by the degree type among the intermetallic compounds all over the visual field range.

[0013]

[Equation 1]

$$\text{数密度 (個/mm}^2\text{)} = \frac{\text{視野中の0.1} \sim \text{0.8} \mu\text{m径化合物数 (個)}}{\text{試料膜厚} \times \text{視野範囲面積 (mm}^2\text{)}}$$

[0014] The Measuring condition of the corrosion current value of sacrificial anode material is as follows. As a reference electrode, a standard calomel electrode is used, brine is used 3.5% as the electrolytic solution, and it is 2 an area of 1cm at the temperature of 40 degrees C. The sample was measured in [trace-speed 20 mV/min and rest potential measuring-time] 5 minutes. Corrosion current values are the anode obtained by doing in this way, and a current value equivalent to the intersection (A or B of drawing 3) of a cathode biparite polar curve. The following approaches estimated the corrosion resistance of a sample. this invention composite sample and a comparison alloy composite sample are used as tube tubing by **** processing, respectively. The fin and the header plate of 1.2mm of board thickness which consist these tube tubing of an aluminum-0.5%Si-0.2%Cu-1.0%Mn-2.0%Zn alloy of 0.07mm of board thickness and which carried out corrugated processing, And the heat exchanger was produced using the side plate (4343 wax material, aluminum alloy composite which consists of core material 3003+0.15%Mg which carried out the clad of the aluminum-1.5%Zn sacrificial anode material by a unit of 10% respectively). The erosion trial which makes the high-speed rate-of-flow liquid collide

to a circulation corrosion test [by the etching fluid of the following 2 type] and tube plate sacrificial anode material side was carried out, and the maximum pitting depth generated from the sacrificial anode material side was measured. These results are shown in Table 2.

[0015] <liquid condition of corrosion test> ** acidity side severe testing liquid type: -- tap water +10ppmCu ion +150ppmCl ion; -- pH3 test condition: -- the cycle trial of 85 degree-Cx 10 hours, and room temperature x 14 hours is performed for five months.

** alkalinity side severe testing liquid type: -- tap water +200ppmCO₃²⁻ ion +50ppmCl ion; -- pH9 test condition: -- the cycle trial of 85 degree-Cx 10 hours, and room temperature x 14 hours is performed for five months.

** erosion corrosion-proof trial liquid type: -- tap water +200ppmCO₃²⁻ ion +50ppmCl ion; -- pH10 condition: -- diameter of nozzle: out of which testing-machine liquid comes -- the 40 degree-Cx1 week continuous corrosion test was performed by 2mmphi and vertical-distance:5mm rate-of-flow 8 m/sec. from a nozzle to a sample.

[0016]

[Table 1]

表 I 合金組成

	合金 No	犧牲材組成						芯材組成								Al
		Zn	Mn	Ge	In	Sn	Si	Si	Cu	Mn	Mg	Cr	Zr	Ti		
本発明例	1	2.2	0.8	—	—	—	—	0.3	0.15	1.1	—	—	0.1	—	残部	
	2	2.5	0.5	—	—	—	—	0.5	0.3	1.0	—	—	—	—	残部	
	3	3.0	0.7	—	—	—	—	0.5	0.5	1.0	—	—	—	—	残部	
	4	2.6	0.5	—	—	—	—	0.8	0.3	1.2	0.1	—	—	—	残部	
	5	3.5	0.8	—	—	—	—	0.8	0.5	1.0	0.1	—	—	—	残部	
	6	4.0	1.0	—	—	—	—	0.8	0.6	1.1	0.1	—	—	—	残部	
	7	5.0	1.0	—	—	—	—	0.8	0.8	1.1	—	—	—	—	残部	
	8	4.2	1.2	—	—	—	—	0.5	0.8	1.1	—	—	—	0.15	残部	
	9	3.0	0.8	—	—	—	—	0.5	0.5	1.1	—	0.1	0.1	0.1	残部	
	10	2.5	0.5	—	—	—	0.5	0.5	0.5	1.2	—	—	—	—	残部	
	11	2.5	1.0	0.2	—	—	0.5	0.8	0.3	1.2	0.1	—	—	—	残部	
	12	3.5	0.7	—	—	—	0.7	0.8	0.5	1.0	0.1	—	—	—	残部	
	13	3.5	0.8	—	—	—	0.3	0.8	0.5	1.0	0.1	—	—	—	残部	
	14	2.5	1.0	—	0.02	—	—	0.5	0.5	1.1	—	—	—	—	残部	
	15	2.2	0.8	—	—	0.03	—	0.5	0.5	1.2	—	—	—	0.1	残部	
比較例	16	2.0	—	—	—	—	—	0.5	0.5	1.0	—	—	—	—	残部	
	17	2.8	0.4	—	—	—	—	0.7	0.4	1.0	—	—	—	—	残部	

[0017]

[Table 2]

表2 製造条件および犠牲材中の化合物数密度、腐食試験でのチューブ最大孔食深さ

	No	製造条件 犠牲材均質化 処理条件	クラフ脱圧延 開始温度	犠牲材のAl-Mn 0.1~0.8 μm 化合物数密度 (個/mm ²)	犠牲材の 腐食電流値 (μA/cm ²)	酸性側腐食試験 チューブ最大孔食深さ (μm)	アルカリ性側腐食試験 チューブ最大孔食深さ (μm)	ED-70試験 チューブ最大孔食 深さ (μm)
本 発 明 例	1	450℃×3hr	480℃	2.5×10^9	20	80	70	70
	2	450℃×3hr	520℃	2.4×10^9	30	70	70	70
	3	440℃×6hr	520℃	2.9×10^9	8	50	60	60
	4	440℃×3hr	490℃	2.4×10^9	7	70	70	70
	5	450℃×3hr	520℃	3.2×10^9	9	50	50	60
	6	450℃×5hr	520℃	3.4×10^9	10	50	50	40
	7	490℃×7hr	530℃	3.5×10^9	12	60	50	40
	8	490℃×4hr	530℃	3.6×10^9	15	60	50	40
	9	440℃×3hr	520℃	3.0×10^9	15	50	60	60
	10	440℃×5hr	470℃	2.8×10^9	20	70	70	60
	11	500℃×5hr	490℃	2.9×10^9	25	70	70	40
	12	450℃×5hr	510℃	3.4×10^9	10	50	50	50
	13	480℃×4hr	510℃	3.2×10^9	10	50	50	60
	14	430℃×4hr	500℃	2.8×10^9	30	60	70	50
	15	430℃×7hr	500℃	2.9×10^9	20	60	60	60
比 較 例	16	450℃×7hr	500℃	なし	150	100	100	貫通
	17	590℃×12hr	530℃	1.5×10^9	100	50	70	貫通
	18	550℃×6hr	540℃	1.8×10^9	120	50	100	貫通

[0018] Also in which corrosion test of an acid environment and an alkaline environment, the pitting depth is 80 micrometers or less, and sample No.1-15 of this invention composite secure the outstanding corrosion resistance so that clearly from Table 2. Furthermore, even when the liquid rate of flow in a tube is large, the chemical dissolution of a front face which serves as an origin of an erosion phenomenon etc. is controlled, and the maximum pitting depth is also 70 micrometers or less as a result. On the other hand, corrosion resistance is inferior in comparison sample No.16 in which an alloy presentation separates from the range of this invention by the acidity side and the alkalinity side test atmosphere, further, an erosion trial also advances notably and corrosion has come to generate a through tube. Moreover, comparison sample No.17 with the low grain density of an aluminum-Mn system intermetallic compound generated the through tube. As mentioned above, aluminum alloy composite sample by this invention acquires the outstanding corrosion resistance to which the sacrifice corrosion prevention ability which was excellent also in the corrosive environment not only an acidity side but by the side of alkalinity is secured to, and corrosion pitting does not advance over a long period of time so that clearly. Also in the environment where erosion tends [furthermore] to advance, it is hard to dissolve a sacrificial anode material front face chemically, and erosion-proof nature can solve the conventional problem and does remarkable effectiveness so on industry, such as being improved sharply.

[0019]

[Effect of the Invention] The corrosion prevention operation by sacrificial anode material is excellent as

aluminium alloy composite for heat exchangers of this invention, and without growing deeply, pitting from the refrigerant side of a heat exchanger can show long-term pitting-proof nature, and can manufacture a heat exchanger with it. [remarkable corrosion resistance and] [high]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to aluminum alloy composite of a three-tiered structure suitable as an ingredient of tube tubing which forms the refrigerant path of the heat exchanger which would stretch in more detail and was formed of law about aluminum alloy composite of the thin meat used for the heat exchanger for automobiles etc.

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PRIOR ART

[Description of the Prior Art] One example of the usual heat exchanger made from aluminum, for example, a radiator, is shown in (b) of drawing 1, and (b). As (b) of drawing 1 is a front view, (b) is the A-A line sectional view of (b) and it is shown in this drawing, this radiator arranges a fin 2 between the tube tubing 1 which lets a refrigerant pass, attaches the header plate 3 in the both ends of the tube tubing 1, assembles a core 4 and comes to attach the resin tank 5 and 5' in the header plate 3 after soldering through packing 6. On a fin 2, in order to prevent pitting generating by the side of a refrigerant in tube tubing at a JIS3003 alloy presentation using the plate around 0.1mm in thickness which carried out extent addition of the Zn 1.5% (especially % that shows a presentation unless it refuses says weight % hereafter.) A brazing sheet with a thickness of 0.3-0.2mm which made the alloy which added Mg etc. sacrificial anode material, and carried out the clad to the JIS3003 alloy presentation inside the alloy core material which added Si, Cu, etc. (refrigerant side) at JIS7072 alloy or it is used. The brazing sheet of the same quality of the material as the tube tubing 1 with a thickness of 1.0-1.3mm is used for the header plate 3.

[0003] These brazing sheets are exposed to an about 580-610-degree C ambient atmosphere at the time of soldering heating, and this diffuses Zn in the above-mentioned sacrificial anode material in a core material. Drawing 2 shows this condition and (b) of drawing 2 of (b) of drawing 2 is after soldering before soldering. Since this Zn diffusion layer carries out priority corrosion, pitting generated from a refrigerant side does not grow deeply, but takes a shallow large pitting gestalt, and comes to show long-term pitting-proof nature. An aluminum-Zn system, an aluminum-Zn-Mg system, or the aluminum-Mg-In system sacrificial anode alloy itself has the description which takes a shallow large pitting gestalt (page foods), further, even after a core material is exposed, sacrificial anode material is preferentially corroded by the potential difference of a core material and these sacrificial anode material, and it prevents the corrosion of a core material according to it.

[0004] As such conventional aluminium alloy composite, Zn and Mn of the specified quantity are made to contain, and the technique using the sacrificial anode material of the aluminium alloy which improved reinforcement is proposed (JP,56-127194,A, 58-113367, etc.). However, Mn in sacrificial anode material is for making potential for the improvement in on the strength into **, and does not aim at corrosion resistance improvement. However, by one side of the board thickness reduction accompanying the latest lightweight-izing, with advanced features of a heat exchanger, the liquid rate of flow inside tube tubing is very quick compared with the former, and corrosion prevention effectiveness sufficient in the above conventional sacrificial anode material is no longer acquired. That is, since a corrosion rate is increased the more the more the liquid rate of flow inside tube tubing becomes quick, development of the aluminium alloy composite material which can respond to this and in which higher corrosion resistance (self-corrosion resistance or sacrifice anti-corrosiveness) is shown is demanded.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The corrosion prevention operation by sacrificial anode material is excellent as aluminium alloy composite for heat exchangers of this invention, and without growing deeply, pitting from the refrigerant side of a heat exchanger can show long-term pitting-proof nature, and can manufacture a heat exchanger with it. [remarkable corrosion resistance and] [high]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the aluminium alloy composite for heat exchangers which raised corrosion resistance further. The purpose of this invention aims still more detailed at providing the bottom of the rise of the liquid rate of flow with the aluminium alloy composite for pile heat exchangers for an erosion corrosion phenomenon at a lifting in the refrigerant side environment of a tube inside.

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MEANS

[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, after specifying Zn of sacrificial anode material, and the amount of Mn By controlling the particle size of the aluminum-Mn system compound in sacrificial anode material, and distribution The corrosion current value accompanying a corrosion prevention operation of sacrificial anode material can be reduced, and this cannot cause erosion corrosion easily under the large environment of the rate of flow. The function of sacrificial anode material is maintained for a long period of time, it finds out raising corrosion resistance sharply and getting, research is further repeated in this knowledge, and it came to make this invention. That is, this invention is Zn to each one side of (1) aluminum alloy core material. 1.0-6.0%, Mn 0.2-2.0% (% shows weight % above.) It contains and they are Remainder aluminum and aluminum alloy which consists of an unescapable impurity in addition to this. And it is number density 2.0×10^9 about the aluminum-Mn system intermetallic compound whose mean particle diameter is 0.1-0.8 micrometers. An individual / mm³ Sacrificial anode material which consists of an aluminum alloy contained above, The aluminium alloy composite for heat exchangers characterized by coming to carry out the clad of the wax material of the aluminum-Si system alloy containing Si of the specified quantity, (2) aluminum alloy of the above-mentioned sacrificial anode material 0.005 - 0.5% of In(s), Sn 0.005 - 0.5%, 0.02 - 1.2% of Si, germanium Aluminium alloy composite for heat exchangers given in (1) term characterized by containing two of one sort or 0.005 - 2.0% of sorts or more, (3) -- the corrosion current value of said sacrificial anode material -- 40microA/cm² The aluminium alloy composite for heat exchangers (1) characterized by being the following or given in (2) terms is offered. [and] Suppressing low the corrosion dissolution (corrosion current) of sacrificial anode material according to this invention, the corrosion prevention of the core material is carried out efficiently, and erosion can be controlled. In this invention, by specifying the magnitude of the aluminum-Mn system compound in sacrificial anode material, and distribution, it is effective in reducing the corrosion current value of sacrificial anode material remarkably, and can be hard to cause erosion corrosion for the inside of a tube also under the large operating environment of the rate of flow of flowing fluid by this, the function of sacrificial anode material can be maintained for a long period of time, and corrosion resistance can be raised sharply.

[0007]

[Embodiment of the Invention] The sacrificial anode material used in this invention is excellent in a corrosion resistance (self-corrosion resistance and sacrifice anti-corrosiveness) operation. Zn in sacrificial anode material may be 1.0 - 6.0%. Corrosive environment enlarges [Zn] the sacrifice corrosion prevention effectiveness enough also in any by the side of acidity or alkalinity. The addition of Zn cannot maintain sacrifice corrosion prevention ability in an acid environment especially at less than 1.0%. In exceeding 6.0%, there is a possibility that there may be a possibility that oxide film depressor effect and the sacrifice corrosion prevention ability maintenance effectiveness may fall sharply in an alkaline environment, and ingredient melting may occur near the interface of sacrificial anode material and a core material depending on the temperature at the time of soldering heating. Zn addition is 2.5% - 4.5% preferably.

[0008] Mn may be 0.2 - 2.0%. Mn regulates aluminum-Mn system compound distribution, and acts on solution of the problem of erosion corrosion. Mn is because there is a possibility of causing the problem of a weld flaw (micro fissure) or a poor bending processing dimension, at less than 0.2% when the above-mentioned effectiveness is not fully demonstrated, but exceeds 2.0% and tube tubing is manufactured by **** processing or bending soldering processing. In this invention, mean particle diameter of the aluminum-Mn system intermetallic compound in sacrificial anode material is set to 0.1-0.8 micrometers, and it is that number density 2.0×10^9 An individual / mm³ Because this compound distribution out of range of the effectiveness which reduces the corrosion current accompanying the corrosion prevention of sacrificial anode material, and controls erosion corrosion is insufficient, it considers as the above. In this invention, by doing in this way, as mentioned above, a sacrifice material corrosion current value can be controlled more remarkably than the value of the conventional sacrificial anode material, and it can decrease. The electrochemistry measurement result of the sacrificial anode material of this invention is shown in drawing 3 as a mimetic diagram. From drawing 3, by controlling distribution of an aluminum-Mn compound in the range of this invention shows that the so-called corrosion current equivalent to the intersection of an anode curve and a cathode curve decreases remarkably. The corrosion current value of sacrifice material is 40microA/cm². If it is the following, the above-mentioned effectiveness will be demonstrated. A and B show the anode of the example of this invention, and the conventional example, and the intersection of a cathode bipartite polar curve among drawing 3, respectively, and this invention has this intersection in left-hand side from a dotted line C (equivalent to 40micro A/cm² of currents). The corrosion resistance which was excellent for a long period of time can be maintained by carrying out the specified quantity selection convention of In, Sn, and the germanium to sacrificial anode material further depending on corrosive environment in this invention. 0.005 - 2.0% of germanium addition is desirable. At less than 0.005%, it becomes difficult for there to be almost no effectiveness which controls oxide film formation of a sacrificial anode material front face under an alkaline environment, therefore to maintain sufficient sacrifice corrosion prevention function. Even if it exceeds 2.0%, the above-mentioned effectiveness not only does not improve any more, but the rolling nature at the time of ingredient manufacture and the yield fall, and the problem on mass production comes out. More desirable germanium addition is 0.2 - 1.5%. The effectiveness of In and Sn addition is the same as that of Zn. Less than by 0.005, the sacrifice effectiveness runs short, when 0.5% is exceeded, the rolling nature at the time of ingredient manufacture falls, and there is a possibility that the problem that a coil end breaks may occur. In addition, these additions are 0.02 - 0.2% preferably. Moreover, if it carries out sacrificial anode material by addition of Si and is, the reinforcement of composite rises, and it contributes to the improvement in endurance of a heat exchanger. Having made the addition into 0.02 - 1.2% has a possibility of causing deep pitting by the simple substance Si, when less than 0.02 are insufficient as for the above-mentioned effectiveness and 1.2% is exceeded. A more desirable addition is 0.3 - 0.7%.

[0009] In this invention, there is especially no limit about a core material. Improvement in on the strength may be aimed at by Si, Cu, and Mn addition based on a 3003 alloy presentation. Cr, Zr, Mg, and Ti may also be suitably added for the purpose of the improvement in on the strength. As wax material in this invention, there is especially no limit, for example, it can use JIS [of an aluminum-Si system]4343, and JIS4045 alloy, JIS4004 alloy, etc.

[0010] Such heat exchanger aluminium alloy composite can be prepared as follows. Control of the aluminum-Mn system intermetallic-compound distribution in sacrificial anode material is realizable by performing homogenization temperature before sacrificial anode material rolling at 440-520 degrees C. It is difficult to equalize an ingot organization at less than 440 degrees C. In carrying out exceeding 520 degrees C, big and rough-ization of a compound becomes active, and it becomes difficult to carry out distribution as the above-mentioned convention of this invention. The holding time in the above-mentioned temperature has 3 - 9 desirable hours. Not only the homogenization temperature of sacrificial anode material but a convention of the clad rolling initiation temperature which is a process after that is important, and clad temperature is good to carry out at 420-520 degrees C. There is a possibility that the phenomenon in which sacrificial anode material separates [this temperature] from a core material at

less than 420 degrees C at the time of clad rolling may come out. Although there is no problem of poor clad sticking by pressure when carrying out exceeding 520 degrees C, it becomes difficult to satisfy compound distribution of the sacrificial anode material specified by this invention. In addition, cold rolling and especially intermediate-annealing conditions are not limited.

[0011] aluminum alloy composite of this invention can be used also for the header plate of a radiator besides radiator tube tubing, in addition if it is the same as that of the purpose of this invention, it can fully be used also as the tube seat of what kind of member, for example, a heater core, or a DORON cup evaporator, and header tubing. In the aluminium alloy composite of this invention, although especially a limit does not have the rate of a clad of sacrificial anode material, 8 - 20% is desirable to all composite board thickness (by thickness), and 12 - 17% is more desirable. Moreover, the rate of a clad of wax material does not differ especially from the conventional thing, but is usually 8 - 12% preferably 5 to 15% to all composites. Although the thickness of the heat exchanger aluminium alloy composite of this invention changes with classes of an application and heat exchanger etc., it is usually 0.2-0.4mm.

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EXAMPLE

[Example] Next, this invention is further explained to a detail based on an example.

Metal mold casting cast 17 kinds of combination alloys of the sacrificial anode material of a presentation, and a core material shown in example 1 table 1, sacrificial anode material homogenized after double-sided facing respectively on the conditions shown in Table 2, and 40mm was made to 5mm in thickness, and a core material only by facing with hot rolling. That is, it was made for the rate of a clad to the whole (for wax material to also be included) composite of sacrificial anode material to become 10%. In addition, comparison sample No.18 in Table 2 are completely the same as that of sample No.3 of this invention except having changed homogenization of sacrificial anode material like a notation in alloy No.3 of this invention. Using JIS4343 alloy, metal mold casting of the wax material was carried out like sacrificial anode material, and after facing, it performed hot rolling and was taken as 5mm thickness. That is, the rate of a clad to the whole composite was made into 10%. Hot rolling was started on the conditions which show repeatedly three sheets, wax material, a core material, and sacrificial anode material, in Table 2 at this order, and it considered as the clad plate with a thickness of 3.5mm of three layers. It considered as 0.29mm thickness with cold rolling after that, and intermediate annealing of 340 degree-Cx 2 hours was given, and, finally it cold-rolled to 0.25mm in thickness, and considered as the sample of H14 material. About aluminum-Mn system intermetallic-compound number density with a mean particle diameter [in sacrificial anode material] of 0.1-0.8 micrometers, the flake was perpendicularly cut [samples / these] down to the rolling direction by the precision cutter (microtome equipment), and it measured with the transmission electron microscope. Then, sample thickness was determined by the fringes of equal thickness, and mean particle diameter calculated the number density of the thing of the aluminum-Mn system compound which is 0.1-0.8 micrometers by the degree type among the intermetallic compounds all over the visual field range.

[0013]

[Equation 1]

$$\text{数密度 (個/mm}^2\text{)} = \frac{\text{視野中の0.1} \sim \text{0.8} \mu\text{m径化合物数 (個)}}{\text{試料膜厚} \times \text{視野範囲面積 (mm}^2\text{)}}$$

[0014] The Measuring condition of the corrosion current value of sacrificial anode material is as follows. As a reference electrode, a standard calomel electrode is used, brine is used 3.5% as the electrolytic solution, and it is 2 an area of 1cm at the temperature of 40 degrees C. The sample was measured in [trace-speed 20 mV/min and rest potential measuring-time] 5 minutes. Corrosion current values are the anode obtained by doing in this way, and a current value equivalent to the intersection (A or B of drawing 3) of a cathode bipartite polar curve. The following approaches estimated the corrosion resistance of a sample. this invention composite sample and a comparison alloy composite sample are used as tube tubing by **** processing, respectively. The fin and the header plate of 1.2mm of board thickness which consist these tube tubing of an aluminum-0.5%Si-0.2%Cu-1.0%Mn-2.0%Zn alloy of 0.07mm of board thickness and which carried out corrugated processing, And the heat exchanger was produced using the side plate (4343 wax material, aluminum alloy composite which consists of core

material 3003+0.15%Mg which carried out the clad of the aluminum-1.5%Zn sacrificial anode material by a unit of 10% respectively). The erosion trial which makes the high-speed rate-of-flow liquid collide to a circulation corrosion test [by the etching fluid of the following 2 type] and tube plate sacrificial anode material side was carried out, and the maximum pitting depth generated from the sacrificial anode material side was measured. These results are shown in Table 2.

[0015] <liquid condition of corrosion test> ** acidity side severe testing liquid type: -- tap water +10ppmCu ion +150ppmCl ion; -- pH3 test condition: -- the cycle trial of 85 degree-Cx 10 hours, and room temperature x 14 hours is performed for five months.

** alkalinity side severe testing liquid type: -- tap water +200ppmCO₃²⁻ ion +50ppmCl ion; -- pH9 test condition: -- the cycle trial of 85 degree-Cx 10 hours, and room temperature x 14 hours is performed for five months.

** erosion corrosion-proof trial liquid type: -- tap water +200ppmCO₃²⁻ ion +50ppmCl ion; -- pH10 condition: -- diameter of nozzle: out of which testing-machine liquid comes -- the 40 degree-Cx1 week continuous corrosion test was performed by 2mmphi and vertical-distance:5mm rate-of-flow 8 m/sec. from a nozzle to a sample.

[0016]

[Table 1]

表1 合金組成

	合金 No	犠牲材組成						芯材組成								Al
		Zn	Mn	Ge	In	Sn	Si	Si	Cu	Mn	Mg	Cr	Zr	Ti		
本発明例	1	2.2	0.8	—	—	—	—	0.3	0.15	1.1	—	—	0.1	—	残部	
	2	2.5	0.5	—	—	—	—	0.5	0.3	1.0	—	—	—	—	残部	
	3	3.0	0.7	—	—	—	—	0.5	0.5	1.0	—	—	—	—	残部	
	4	2.6	0.5	—	—	—	—	0.8	0.3	1.2	0.1	—	—	—	残部	
	5	3.5	0.8	—	—	—	—	0.8	0.5	1.0	0.1	—	—	—	残部	
	6	4.0	1.0	—	—	—	—	0.8	0.6	1.1	0.1	—	—	—	残部	
	7	5.0	1.0	—	—	—	—	0.8	0.8	1.1	—	—	—	—	残部	
	8	4.2	1.2	—	—	—	—	0.5	0.8	1.1	—	—	—	0.15	残部	
	9	3.0	0.8	—	—	—	—	0.5	0.5	1.1	—	0.1	0.1	0.1	残部	
	10	2.5	0.5	—	—	—	0.5	0.5	0.5	1.2	—	—	—	—	残部	
	11	2.5	1.0	0.2	—	—	0.5	0.8	0.3	1.2	0.1	—	—	—	残部	
	12	3.5	0.7	—	—	—	0.7	0.8	0.5	1.0	0.1	—	—	—	残部	
	13	3.5	0.8	—	—	—	0.3	0.8	0.5	1.0	0.1	—	—	—	残部	
	14	2.5	1.0	—	0.02	—	—	0.5	0.5	1.1	—	—	—	—	残部	
	15	2.2	0.8	—	—	0.03	—	0.5	0.5	1.2	—	—	—	0.1	残部	
比較例	16	2.0	—	—	—	—	—	0.5	0.5	1.0	—	—	—	—	残部	
	17	2.8	0.4	—	—	—	—	0.7	0.4	1.0	—	—	—	—	残部	

[0017]

[Table 2]

表2 製造条件および犠牲材中の化合物数密度、腐食試験でのチューブ最大孔食深さ

	No	製造条件		犠牲材のAl-Mn 0.1 ~ 0.8 μm 径化合物数密度 (個/ mm^2)	犠牲材の 腐食電流値 ($\mu\text{A}/\text{cm}^2$)	酸性側腐食試験 チューブ最大孔食深さ (μm)	アルカリ性側腐食試験 チューブ最大孔食深さ (μm)	ID-フロン試験 チューブ最大孔食 深さ (μm)
		犠牲材均質化 処理条件	クラフト熱圧延 開始温度					
本発明例	1	450 $^{\circ}\text{C} \times 3\text{hr}$	480 $^{\circ}\text{C}$	2.5×10^9	20	80	70	70
	2	450 $^{\circ}\text{C} \times 3\text{hr}$	520 $^{\circ}\text{C}$	2.4×10^9	30	70	70	70
	3	440 $^{\circ}\text{C} \times 6\text{hr}$	520 $^{\circ}\text{C}$	2.9×10^9	8	50	60	60
	4	440 $^{\circ}\text{C} \times 3\text{hr}$	490 $^{\circ}\text{C}$	2.4×10^9	7	70	70	70
	5	450 $^{\circ}\text{C} \times 3\text{hr}$	520 $^{\circ}\text{C}$	3.2×10^9	9	50	50	60
	6	450 $^{\circ}\text{C} \times 5\text{hr}$	520 $^{\circ}\text{C}$	3.4×10^9	10	50	50	40
	7	490 $^{\circ}\text{C} \times 7\text{hr}$	530 $^{\circ}\text{C}$	3.5×10^9	12	60	50	40
	8	490 $^{\circ}\text{C} \times 4\text{hr}$	530 $^{\circ}\text{C}$	3.6×10^9	15	60	50	40
	9	440 $^{\circ}\text{C} \times 3\text{hr}$	520 $^{\circ}\text{C}$	3.0×10^9	15	50	60	60
	10	440 $^{\circ}\text{C} \times 5\text{hr}$	470 $^{\circ}\text{C}$	2.8×10^9	20	70	70	60
	11	500 $^{\circ}\text{C} \times 5\text{hr}$	490 $^{\circ}\text{C}$	2.9×10^9	25	70	70	40
	12	450 $^{\circ}\text{C} \times 5\text{hr}$	510 $^{\circ}\text{C}$	3.4×10^9	10	50	30	50
	13	480 $^{\circ}\text{C} \times 4\text{hr}$	510 $^{\circ}\text{C}$	3.2×10^9	10	50	50	60
	14	430 $^{\circ}\text{C} \times 4\text{hr}$	500 $^{\circ}\text{C}$	2.8×10^9	30	60	70	50
	15	430 $^{\circ}\text{C} \times 7\text{hr}$	500 $^{\circ}\text{C}$	2.9×10^9	20	60	60	60
比較例	16	450 $^{\circ}\text{C} \times 7\text{hr}$	500 $^{\circ}\text{C}$	なし	150	100	100	貫通
	17	590 $^{\circ}\text{C} \times 12\text{hr}$	530 $^{\circ}\text{C}$	1.5×10^9	100	60	70	貫通
	18	550 $^{\circ}\text{C} \times 6\text{hr}$	540 $^{\circ}\text{C}$	1.8×10^9	120	50	100	貫通

[0018] Also in which corrosion test of an acid environment and an alkaline environment, the pitting depth is 80 micrometers or less, and sample No.1-15 of this invention composite secure the outstanding corrosion resistance so that clearly from Table 2. Furthermore, even when the liquid rate of flow in a tube is large, the chemical dissolution of a front face which serves as an origin of an erosion phenomenon etc. is controlled, and the maximum pitting depth is also 70 micrometers or less as a result. On the other hand, corrosion resistance is inferior in comparison sample No.16 in which an alloy presentation separates from the range of this invention by the acidity side and the alkalinity side test atmosphere, further, an erosion trial also advances notably and corrosion has come to generate a through tube. Moreover, comparison sample No.17 with the low grain density of an aluminum-Mn system intermetallic compound generated the through tube. As mentioned above, aluminum alloy composite sample by this invention acquires the outstanding corrosion resistance to which the sacrifice corrosion prevention ability which was excellent also in the corrosive environment not only an acidity side but by the side of alkalinity is secured to, and corrosion pitting does not advance over a long period of time so that clearly. Also in the environment where erosion tends [furthermore] to advance, it is hard to dissolve a sacrificial anode material front face chemically, and erosion-proof nature can solve the conventional problem and does remarkable effectiveness so on industry, such as being improved sharply.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The front view and (b) which show an example of the radiator of the former [(b)] are the A-A line sectional view of (b).

[Drawing 2] It is the explanatory view of the diffusion condition to the inside of the core material of Zn in sacrificial anode material, and (b) shows soldering before and (b) shows the soldering back.

[Drawing 3] It is the graph which showed the electrochemical measurement result of the sacrificial anode material of this invention by the comparison with the conventional thing.

[Translation done.]

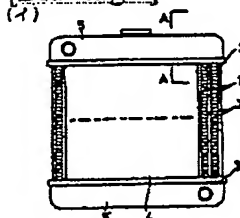
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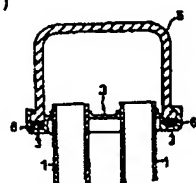
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DRAWINGS

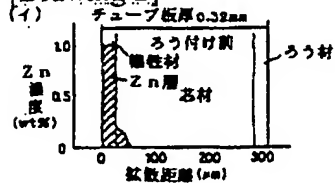
[Drawing 1]



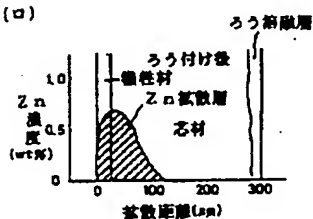
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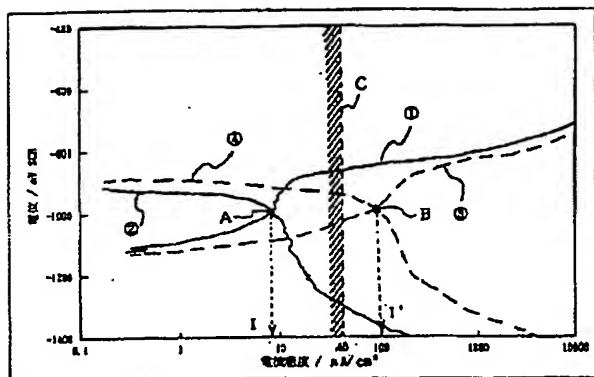
[Drawing 2]



(ロ)



[Drawing 3]



(注)

- ①本発明例犠牲材のアノード曲線
 ②本発明例犠牲材のカソード曲線
 ③従来例犠牲材のアノード曲線
 ④従来例犠牲材のカソード曲線
 ⑤斜線部の左側は本発明範囲を示す。
- 上図の $I \mu A/cm^2$: 本発明例犠牲材の腐食電流値
 上図の $I' \mu A/cm^2$: 従来例犠牲材の腐食電流値

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